

A Dynamic Analysis Model for Stress Decay in Emulsions under Steady Shear Rate

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A dynamic model containing four parameters and based on the law of mass action, was formulated for the characterization of stress decay in emulsions during a start-shear experiment. NaCl or one of two salt mixtures was added to an emulsion containing 1.0% of gelatine to test the model. Salt presence, pH and, to a lesser extent, salt concentration and salt type, affected the parameter values. The model fitted the experimental data successfully.

Introduction

The measurement values obtained within the first few minutes are probably of primary importance if sensory-instrumental correlations are the aim in a rheological measurement (1, 2). A stress decay that follows a stress overshoot is a typical response in start-shear experiments (i.e. shear stress-time curves recorded at constant shear rate) conducted on food emulsions (3, 4). According to van den Tempel (5), this behaviour is a common property of non-linear viscoelastic materials, which can be derived from a competition between the breaking and reformation of junctions in a temporary network structure. The overshoot phenomenon appears to be independent of the mechanism responsible for elasticity, which suggests that widely differing materials have common structural elements which are responsible for the behaviour observed (5).

Elliott and Green (6) presented ideal elasticity and first-order kinetics as models for stress overshoot and stress decay in emulsions. Instead of ideal elasticity, however, emulsions exhibit a non-linear stress-time behaviour at inception of steady shear; in addition, only partial strain recovery appears in most emulsions upon removal of the stress. Other theoretical (5) or empirical models (1, 2, 7-11) have thus been used to obtain a better fit with experimental data. In this study, an attempt is made to describe the stress decay semi-empirically, on the basis of a simplified breakdown mechanism.

Model development

If the junctions which, for most emulsions, are maintained by physical rather than covalent bonds, exist in either of two states, active (S_A) or inactive (S_I), the relationship



can be assumed to prevail between the proportions of the states under a constant shear rate. Assuming that k_1 and k_2 are first-order rate constants for inactivation and reactivation, the following equations provide a model for the breakdown of structure according to the law of mass action (12):

$$\frac{dS_A}{dt} = -k_1 S_A + k_2 S_I \quad \text{Eqn [1]}$$

$$S_A + S_I = S_A(0) \quad \text{Eqn [2]}$$

$$S_I(0) = 0 \quad \text{Eqn [3]}$$

The breakdown is thus considered to begin from the initial time $t = 0$. If shear stress $\tau(t)$ is proportional to $S_A(t)$, Eqns [1] and

[2] can be rewritten as

$$\frac{d\tau}{dt} = -k_1 \tau + k_2(\tau_0 - \tau) \quad \text{Eqn [4]}$$

where τ_0 is the maximum shear stress which could be reached if all the junctions were in the active state. Assuming the initial condition $\tau(t_0) = \tau_0$, the solution of Eqn [4] is

$$\tau = \tau_0 e^{-(k_1+k_2)(t-t_0)} + \frac{k_2 \tau_0}{k_1+k_2} [1 - e^{-(k_1+k_2)(t-t_0)}] \quad \text{Eqn [5]}$$

which is consistent with the measured values of τ at times $t \geq t_0$, as presented in Fig. 1. Considering that

$$t_0 = \frac{\tau_0}{G^* \dot{\gamma}} \quad \text{Eqn [6]}$$

where G^* is the modulus of deformation during the linear part of the stress-time curve, Eqn [5] becomes

$$\tau = \tau_0 e^{-(k_1+k_2)\left(t - \frac{\tau_0}{G^* \dot{\gamma}}\right)} + \frac{k_2 \tau_0}{k_1+k_2} [1 - e^{-(k_1+k_2)\left(t - \frac{\tau_0}{G^* \dot{\gamma}}\right)}] \quad \text{Eqn [7]}$$

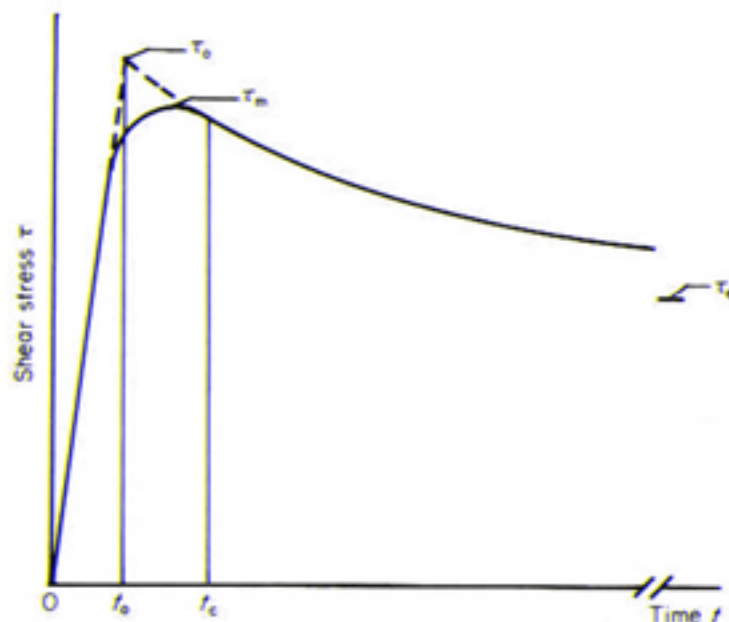


Fig. 1 Determination of the point (t_0, τ_0) in an emulsion containing no added salt, at pH 5.5